

**Anticorrosive Black Coating on Zinc Alloy and Method for Making
Same**

[Couche noire anticorrosive sur un alliage de zinc et son
procédé de préparation]

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The invention relates to a black anticorrosive coating formed of two strata on a zinc alloy and a method for making this anticorrosive layer.

In order to protect them from corrosion, metal surfaces, such as steel surfaces, are coated with a zinc alloy (e.g., Zn-Fe, Zn-Ni, Zn-Co, Zn-Mn). The zinc alloy deposit can then be protected by a chromating layer. The latter may be obtained by processing the zinc alloy deposit with a solution containing Cr^{6+} . However, the use of solutions containing Cr^{6+} is no longer desirable due to toxicity and environmental protection concerns. U.S. Patent 5,415,702 proposes, by way of a substitute, the processing of a zinc/nickel or zinc/iron alloy with an acid solution that includes Cr^{3+} ions and phosphate ions. The surface thereby coated in chromate may be brought into contact with an alkaline metal silicate solution. Lastly, in another step, one may deposit an organic coating onto the obtained silicate layer (e.g., a paint).

This method involves the following disadvantages: the corrosion protection of a layer prepared using this method on a zinc/iron alloy is not sufficient in relation to that of a layer prepared using this method on a zinc/nickel alloy. Moreover, the

¹ Numbers in the margin indicate pagination in the foreign text.

corrosion protection of a layer prepared using this method on a zinc/iron alloy is defective after being heated for one hour to a temperature beyond 150 degrees C (thermal shock). Lastly, due to the silicate-based coating, undesirable white traces on the surface may be produced after a certain amount of time has elapsed. Additionally, the surface prepared using this method offers insufficient adhesion for another coat of paint at a later date.

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The present invention aims to remedy the disadvantages of the state of the art, to further improve the protection against corrosion of zinc alloys, and to yield an anticorrosive black coating on zinc alloys that has, after being heated for one hour up to 120 degrees C or up to 150 degrees C or, in certain cases, beyond this temperature (thermal shock), and following a salt mist test according to Standard DIN 50 021, a resistance to corrosion that lasts longer than 200 hours. The invention also aims to give the anticorrosive coating a uniform black appearance that does not change over time.

The method of the invention is characterized in that it consists of treating the zinc alloy in a first step with an aqueous Cr^{3+} aqueous solution, containing a complexing agent or several complexing agents, and in treating the thereby-passivated zinc alloy in a second step of the method with an

aqueous solution containing an organic polymer, an anticorrosive metal oxide, and optionally a black pigment. The anticorrosive coating realized on a zinc alloy of the invention is composed of a superposition of two individual layers, prepared according to a method of the invention, with the first layer having a coating weight (expressed in Cr) of 1 to 4 mg/dm².

The method described according to the invention is composed of two steps. In the first step, the alloyed zinc deposit is treated with a Cr³⁺ aqueous acid solution, free of Cr⁶⁺, which includes one or several complexing agents. The deposit is thereby passivated. The duration of treatment ranges from 20 to 400 seconds. A preferred duration of treatment ranges from 60 to 240 seconds. In the second step of the method, the passivated zinc alloy, rinsed and drained, is treated with an aqueous suspension that includes organic polymers, anticorrosive metal oxides, and optionally black pigments. The duration of treatment ranges from 5 to 120 seconds. Lastly, the treated zinc alloy may be dried in hot air (for example, at between 50 and 75 degrees C, preferably 70 degrees C).

The pH of the Cr³⁺ acid solution will range from 1 to 4, preferably from 1 to 3. The pH is preferably adjusted using mineral acids such as HNO₃, H₂SO₄, HCl, or H₃PO₄.

Treatment of the zinc alloy with the passivation solution and by the suspension can be performed in various ways, e.g.,

by immersion, by projection, or using a brush or roller.

Application by immersion is the preferred method. The temperature of the Cr^{3+} solution used in the first step of the method ranges from 20 to 80 degrees C, preferably from 25 to 60 degrees C; the temperature of the aqueous suspension used in the second step of the method ranges from 15 to 35 degrees C, preferably from 20 to 30 degrees C.

Trivalent chromium may be placed inside the solution in the form of trivalent chromium salts such as, for example $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, chromium (III) acetate, or in the form of trivalent chromium sulfate ("pure" chromium sulfate or chromium sulfate and other cations such as, for example $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$). According to another possibility, one may prepare a solution of Cr^{3+} starting with a solution of Cr^{6+} with addition of a mineral acid in the presence of a reducing agent such as, for example, formaldehyde or sodium hydrogensulfite. The lower limit for the chromium content of the solution (expressed as Cr^{3+}) is 1 g/l (which corresponds to 0.02 mol/l), preferably 5 g per liter (which corresponds to 0.1 mol/l); the upper limit for the chromium (III) content of the solution is 30 g/l (which corresponds to 0.58 mol/l), but preferably 20 g/l (which corresponds to 0.38 mol/l).

In order to complex the Cr^{3+} ions and thereby regulate the precipitation of chromium III hydroxide onto the surface of the part during the conversion operation, the solution contains one or several complexing agents such as phosphates, hypophosphites, organic acid salts (e.g., citric acid, oxalic acid, tartaric acid, malonic acid, malic acid, formic acid, acetic acid, lactic acid, aminoacetic acid, iminodiacetic acid) or urea.

Phosphates are preferably used because they encourage especially well the formation of a dark conversion layer. Phosphates act as a "proton reservoir;" these protons activate and maintain the passivation process of the alloyed zinc deposit. Phosphates will be incorporated, for example, in the form of Na_3PO_4 , Na_2HPO_4 , NaH_2PO_4 , or in the form of phosphoric acid. Phosphates may be present for a minimal concentration in the solution (expressed as PO_4^{3-}) of 10 g/l (which corresponds to 0.01 mol/l), preferably 15 g/l (which corresponds to 0.15 mol/l). The upper limit of the phosphate concentration in the solution is preferably 44 g/l (which corresponds to 0.42 mol/l), preferably 25 g/l (which corresponds to 0.26 mol/l).

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Hypophosphite may be added (for example, in the form of an alkaline metal hypophosphite such as NaH_2PO_2 or in the form of hypophosphorous acid), alone or preferably along with phosphates. One advantageous effect of hypophosphite involves

the fact that it delays precipitation of the chromium hydroxide in the solution onto the zinc alloy surface up to a pH of 4.5. Without adding hypophosphite, chromium hydroxide precipitates once the solution reaches a pH of 3.0. The minimal concentration of hypophosphite (expressed as H_2PO_2) is 0.08 mol/l, and preferably 0.23 mol/l. The upper limit of the hypophosphite concentration is 0.65 mol/l and preferably 0.5 mol/l, even more preferably 0.45 mol/l.

The other complexing agents mentioned may be incorporated at up to 0.025 mol/l to 0.6 mol/l, with a preferably for the interval ranging from 0.06 to 0.2 mol/l. It is preferable to use them along with phosphates and/or hypophosphite.

The protection against corrosion and the uniformity of the black color may be further improved by adding ions of iron, molybdenum, cobalt, and/or nickel to the Cr^{3+} solution. The quantities to add may range, for example, from 0.001 mol/l to 0.1 mol/l.

The corrosion protection and adhesion of the finishing layer may be improved by incorporating silicon dioxide into the passivation solution in the form of colloidal particles such as, the Ludox AM30 dispersion marketed by the Du Pont Company. The incorporated quantity may range from 0.07 mol/l and 1.3 mol/l.

The passivation layer, or 1st stratum, has a thickness that ranges from 0.5 to 5 μ , preferably between 0.5 μ and 1.5 μ .

The aqueous solution used in the second step of the method includes organic polymers, anticorrosive metal oxides, and optionally black pigments.

The organic polymers used are of the acrylic, methacrylic copolymer type, or vinyl resins. These are polymers of the

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ester of acrylic acid or methacrylic acid and they may have, as an alcohol component, an alkyl group non-substituted or substituted by functional groups, e.g., a methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert-butyl, pentyl, and hexyl group and their higher isomers and homologues, 2-ethylhexyl, phenoxyethyl, hydroxyethyl, 2-hydroxypropyl, caprolactone-hydroxyethyl or dimethylaminoethyl. Commercially-available acrylate copolymers are, for example Lugalvan DC by BASF Company or Carboset 560 by BF Goodrich Company.

As organic polymers, one may also use polyethylene waxes (in the form of an emulsion, e.g., Polygene PE by BASF Company or Luciwax EN 41 by the Morton Company). Waxes advantageously increase the wear resistance of the surfaces and yield, depending upon the wax used, advantageous slip properties such as a low friction coefficient ranging from 0.08 to 0.18. Using appropriate waxes in the suspension yields constant friction coefficients at ± 0.03 .

The quantity of organic polymers added (expressed respectively as dry matter) totals 5 to 150 g/l, preferably 10 to 100 g/l. A combination of 5 to 90 g/l of acrylate or methacrylate copolymer and 1 to 60 g/l of polyethylene wax has had very positive results.

As anticorrosive metal oxides, one may use silicon dioxide, titanium dioxide, zirconium dioxide, and/or rare earth oxides such as cerium oxide or La_2O_3 or Y_2O_3 or Pr_6O_{11} . These metal oxides are preferably used in the form of an aqueous solution of nanoparticles. The concentration of the metal oxides (in relation to solid matter) in the aqueous suspension used in the second step of the method is preferably 20 to 60 g/l with a preference for the interval ranging from 30 to 45 g/l. The metal oxides are fixed by the organic polymers. The introduction of mineral substances into the anticorrosive coating in this form has, in relation to the known treatment using solutions of these substances (e.g., sodium silicate solutions), the advantage of improving the protection against corrosion and maintaining the uniform black color of the anticorrosive coating over time.

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The uniform black appearance of the anticorrosive coating may be further reinforced by the addition of black carbon black pigments (e.g., Derussol P130 by the Degussa Company) or other pigments such as Noir Sanodal marketed by the Clariant Company

to the aqueous solution used during the second step of the method. Preferably, the concentration of carbon black pigments in the aqueous suspension ranges from 5 to 20 g/l.

The friction coating, or the second stratum deposited during the second step, has a thickness of 0.5 to 5 μ , preferably 0.5 to 2.5 μ . The anticorrosive coating thereby has, overall, a thickness that generally ranges from 1 μ to 5 μ , preferably from 1 μ and 4 μ .

The anticorrosive coating made in two steps according to the just-described method of the invention on galvanized metal surfaces has a coating weight in the first stratum (expressed in Cr) of 0.5 to 4 mg/dm². In order to determine this weight, we dissolve the chromium coating (first stratum) formed on the galvanized metal surface following the first step of the method (passivation) with 10% hydrochloric acid and we determine the chromium content using atomic absorption spectroscopy. The second stratum of the anticorrosive coating is composed of anticorrosive metal oxides, black pigments, and, if desired, other additives incorporated into organic polymers. One advantage of this anticorrosive coating of the invention resides in the absence of Cr⁶⁺ and in corrosion resistance after being heated for one hour to 120 degrees C or to 150 degrees C, and a salt mist resistance according to Standard DIN 50 021 of 200 hours and sometimes well beyond the latter.

The invention is described in greater detail by way of the following examples:

Example 1

We dissolve 19 g of CrO_3 in roughly 250 ml of water. We very slowly add 11 g of 96% H_2SO_4 . We then add 60 g of 85% H_3PO_4 and add water until 1 l of solution is reached. The temperature of the solution rises to about 65 degrees C. The solution is maintained while stirring; we then carefully add formaldehyde

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until the color changes to yellow-green. We cool it to about 25 degrees C. To this Cr^{3+} solution, we add per liter 30 g of sodium hypophosphite and then 20 g of citric acid. The pH is adjusted to 2.7 by a 50% NaOH solution and the mixture is kept at a temperature of 25 degrees C.

The aqueous solution for making the second coating is composed of 90 g/l of a 44% colloidal dispersion of silicon dioxide particles in water (Ludox AS 40 by the Du Pont Company), 50 g/l of a 27% acrylic copolymer (Carboset 560 by the BF Goodrich Company), and 70 g/l of an ethylenic graft acrylic copolymer (Lugalvan DC by the BASF Company). In order to reinforce the black appearance of the surface treated with the suspension, we add as a black pigment into the aqueous solution 50 g/l of a 20% carbon black dispersion (Derussol P 130 by the Degussa Company).

We coat standard steel plates measuring 100 mm x 70 mm in a conventional manner with a zinc/iron alloy (Fe 0.5%), we activate them in a nitric acid solution at 5 ml/l, then after rinsing we place them for about 180 seconds in the Cr^{3+} solution (solution temperature 25 degrees C), we rinse them, drain them in an air current (room temperature), soak them for about 30 seconds in the aqueous suspension, and dry them for about 15 minutes in a hot air current (70 degrees C). The appearance of the plates is then a uniform black color. The chromium content of the anticorrosion coating is (prior to treatment with the aqueous solution) 2 mg/dm². The treated steel plates are brought to 150 degrees C (thermal shock) for 1 hour and they then undergo a salt mist test per Standard DIN 50 021. White rust is seen to appear after 300 hours.

Example 2

We dilute 60 g of a chromium nitrate solution (chromium content 11.5 %) in 200 ml of water. To it, we add 20 g of 85% phosphoric acid, 0.3 g of 69% nitric acid, and 75 g of colloidal silica dispersion of the Ludox AM 30 type and the volume is adjusted to 1 liter using water. The pH is set to between 1.5 and 1.6 using a 50% NaOH solution.

In conventional fashion, we coat standard steel plates

measuring 100 mm x 70 mm with a zinc/nickel alloy (Ni 12 to 15%), we soak them for about 90 seconds in the Cr^{3+} solution (solution temperature 25 degrees C), we rinse them, drain them in an air current (room temperature), soak them for about 30 seconds in the aqueous suspension (of Example 1), and dry them for about 10 minutes in a hot air current (70 degrees C). The appearance of the plates is then a uniform black color. The chromium content of the anticorrosion coating is (prior to treatment with the aqueous solution) $> 2 \text{ mg/dm}^2$. The treated steel plates are brought to 120 degrees C (thermal shock) for 1 hour and they then undergo a salt mist test per Standard DIN 50 021. The parts do not show any white rust after 240 hours and no red rust after 800 hours.

Example 3

The Cr^{3+} solution is composed of 55 g/l of Chromitan (trademark) (chromium (III) sulfate-based salt), which corresponds to a Cr^{3+} content in the solution of 9.35 g/l, 25.5 g/l of H_3PO_4 , 30 g/l of sodium hypophosphite, 20 g/l citric acid, and 0.9 g/l of HNO_3 , the pH of the solution is adjusted to 2.5 using a 20% NaOH solution.

The aqueous solution for making the second coating is composed of 90 g/l of a 44% colloidal dispersion of silicon dioxide particles in water (Ludox AS 40 by the Du Pont Company), 50 g/l of a 27% acrylic copolymer (Carboset 560 by the BF

Goodrich Company), and 70 g/l of an ethylenic graft acrylic copolymer (Cugalvan DC by the BASF Company).

We coat standard steel plates measuring 100 mm x 70 mm in a conventional manner with a zinc/iron alloy (Fe 0.5%), we clean them, place them for about 240 seconds in the Cr^{3+} solution (solution temperature 25 degrees C), we rinse them, drain them in an air current (room temperature), soak them for about 30 seconds in the aqueous suspension described above, and dry them for about 15 minutes in a hot air current (70 degrees C). The appearance of the plates is then a uniform black color. The chromium content of the anticorrosion coating is (prior to treatment with the aqueous solution) greater than 2 mg/dm². The treated steel plates are brought to 120 degrees C (thermal shock) for 1 hour and they then undergo a salt mist test per Standard DIN 50021. The parts do not show any white rust after 320 hours.

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Example 4

We dissolve 45 g (corresponding to a Cr^{3+} content of 7.65 g) of Chromitan (trademark) (chromium (III) sulfate-based salt) in 500 ml of water, and bring the pH to greater than 5 by adding a 20% NaOH solution. To this solution, we add 45 g of sodium hypophosphite and 54 g of 85% phosphoric acid and the solution is brought up to 1 l by adding water.

The solution is filtered on a filter paper whose pore diameter is 100 μm and it is brought to 60 degrees C for 2 hours. The pH is set to between 2.3 and 2.5 by a 50% NaOH solution. To this solution, we add 1 g of cobalt sulfate, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$.

We coat standard steel plates measuring 100 mm x 70 mm in a conventional manner with a zinc/iron alloy (Fe 0.5%), we activate them in a nitric acid solution at 5 ml/l, we soak them for about 60 seconds in the Cr^{3+} solution (solution temperature 25 degrees C), we rinse them and drain them in an air current (room temperature). The appearance of the plates is then a uniform black color. The chromium content of the anticorrosion coating is greater than 2 mg/dm^2 .

The treated steel plates are placed inside the aqueous solution (Example 1) and they are dried for about 15 minutes in a hot air current (70 degrees C), they are brought to 120 degrees C (thermal shock) for 24 hours and they then undergo a salt mist test per Standard DIN 50021. After 300 hours, no white rust is seen.

Example 5

We dissolve 100 g of $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in 200 ml of water. We dissolve 20 g of NaOH in about 100 ml and add them together. We bring it to 80 degrees C for 1 hour. After cooling to about 25 degrees C, we add 20 g of sodium hypophosphite, 20 g of citric

acid, 15 g of 85% phosphoric acid, 0.6 g of 69% nitric acid, and 100 of silica dispersion of the Ludox AM30 type, and then bring the solution to a volume of 1 l with water. The pH of the solution is 2.5.

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We coat standard steel plates measuring 100 mm x 70 mm in a conventional manner with a zinc/iron alloy (Fe 0.5%), we activate them in a nitric acid solution at 5 ml/l, we soak them for 180 seconds in the Cr^{3+} solution (solution temperature 25 degrees C), we rinse them and drain them in an air current (room temperature). The appearance of the plates is then a uniform black color. The chromium content of the anticorrosion coating ranges from 2 to 4 mg/dm².

The treated steel plates are placed inside the aqueous solution (Example 1) and they are dried for about 15 minutes in a hot air current (70 degrees C), they are brought to 120 degrees C (thermal shock) for 24 hours and they then undergo a salt mist test per Standard DIN 50 021. After 200 hours, no white rust is seen.

Example 6

We add 35 g of a chromium nitrate solution (chromium content 11.5%) to 100 ml of water. To it, we add 6.5 g of NaOH, 15 g of oxalic acid, and 2 g of malonic acid. The temperature rises to above 60 degrees C. After cooling to 25 degrees C, we

add 2 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and we bring the solution volume to 1 l by adding water. The pH is set at 1.5.

We coat standard steel plates measuring 100 mm x 70 mm in a conventional manner with a zinc/nickel alloy (Ni 15%) 12 μm thick, we soak them for 75 seconds in the Cr^{3+} solution (solution temperature 25 degrees C), we rinse them and drain them in an air current (room temperature). The appearance of the plates is then a uniform black color. The chromium content of the anticorrosion coating is 2 mg/dm^2 .

The treated steel plates are placed inside the aqueous solution (of Example 3) for about 30 seconds and they are dried for about 15 minutes in a hot air current (70 degrees C).

The plates are then brought to 120 degrees C (thermal shock) for 1 hour and they then undergo a salt mist test per Standard DIN 50 021. After 200 hours, no white rust is seen and after 800 hours no red rust is seen.

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CLAIMS

1. Method for depositing a black anticorrosive coating onto a zinc alloy, characterized in that it consists of treating the zinc alloy in a first step of the method with an aqueous acid solution of Cr^{3+} , free of Cr^{6+} , containing a complexing agent or several complexing

agents, and of treating the passivated zinc alloy in a second step of the method with an aqueous solution containing an organic polymer, an anticorrosive metal oxide, and optionally a black pigment.

2. Method according to Claim 1, characterized in that, in the first step of the method, the pH of the Cr^{3+} solution ranges from 1 to 4.
3. Method according to Claim 2, characterized in that, in the first step of the method, the pH of the Cr^{3+} solution ranges from 1.0 to 3.0.
4. Method according to one of claims 1 through 3, characterized in that it consists of using, as a complexing agent, a phosphate, a hypophosphite, citric acid, oxalic acid, tartaric acid, malonic acid, malic acid, formic acid, acetic acid, lactic acid, aminoacetic acid, iminodiacetic acid, or urea.
5. Method according to one of claims 1 through 4, characterized in that it consists of adding to the Cr^{3+} solution, in the first step of the method, Fe, Co, Mo, and/or Ni ions in a quantity ranging from 0.001 mol/l to 0.1 mol/l.
6. Method according to one of claims 1 through 5, characterized in that it consists of adding to the Cr^{3+} solution, in the first step of the method, colloidal

particles of silicon dioxide in a quantity [remainder of Claim 6 missing]

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7. Method according to one of claims 1 through 6, characterized in that it consists of using as organic polymers copolymers of acrylate or methacrylate, polyethylene wax, or vinyl resins.
8. Method according to one of claims 1 through 7, characterized in that it consists of using as anticorrosive metal oxides silicon dioxide, titanium dioxide, or rare earth oxides.
9. Method according to one of claims 1 through 8, characterized in that the anticorrosive metal oxides take the form of a suspension of nanoparticles.
10. Anticorrosive black coating on a zinc alloy, characterized in that it includes two strata, in that it is prepared by a method according to one of claims 1 through 8, and in that the first stratum has a weight (expressed as Cr) ranging from 1 to 4 mg/dm².
11. Coating according to Claim 10, characterized in that its thickness ranges from 1 μ to 4 μ .